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GLYCINE-NITRATE SYNTHESIS OF PARTIALLY YTTRIUM-STABILIZED ZIRCONIUM NANOPOWDERS FOR HARD CERAMICS

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The optimal conditions for synthesizing zirconium dioxide nanopowders (partially stabilized by yttrium, 3 mol.% Y_2O_3) by the glycine-nitrate method and the regimes for obtaining high-strength ceramic from the nanopowders by semidry pressing and sintering are determined.
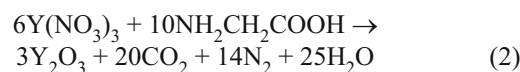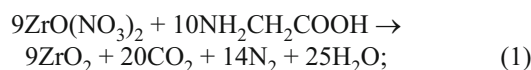
Key words: partially stabilized zirconium dioxide, nanopowders, glycine-nitrate method, ceramic, machining, pressing, sintering.

Materials based on zirconium dioxide partially stabilized by yttrium, magnesium and calcium oxides are used in the fabrication of high-density, high-strength ceramic, refractories and composites for special purposes [1].

Considering the multistage nature of ceramic technology as well as the numerous, often contradictory specifications for powders for high-strength ($\sigma_b \geq 700$ MPa) ceramic (high chemical purity and dispersity, low agglomerability, spheroidal particles, sinterability and others) the methods used to synthesize precursors should make it possible to obtain high-quality powders of partially stabilized zirconium dioxide (PSZD) at the initial stage of the ceramic technology, especially if their consolidation is done by semidry pressing and sintering (SPS). It should be noted that the choice of the method of synthesis, especially the 'solution' method, is largely due to the nature of the initial zirconium compound. Thus, the hydrothermal [2] and so-called 'spray' [3, 4] methods make it possible to obtain high-quality PSZD powders, including nanosize powders, and mechanically strong ceramic; precipitation from solutions, which method is widely used in industrial practice, is not suitable of these purposes [5].

The basic rules for synthesizing ZrO_2 nanopowders (8 mol.% Y_2O_3) from zirconium oxynitrate by the glycine-nitrate method, which is a combination of the 'solution' and thermal' variants, are discussed in [6]. At the first stage nitrate compounds of zirconium and yttrium are dissolved in water together with glycine (α-aminoacetic acid) and the solution is evaporated to a gel state. At the second stage the gel is subjected to heat-treatment, during which it burns and a mixed oxide is formed. According to [6], in this method the

glycine plays a dual role: it forms complexes with metal cations (it prevents precipitation during evaporation and secures a uniform distribution of a stabilizing additive)

$$9ZrO(NO_3)_2 + 10NH_2CH_2COOH \rightarrow$$
$$9ZrO_2 + 20CO_2 + 14N_2 + 25H_2O; \qquad (1)$$

$$6Y(NO_3)_3 + 10NH_2CH_2COOH \rightarrow$$
$$3Y_2O_3 + 20CO_2 + 14N_2 + 25H_2O \qquad (2)$$

and serves as fuel for the combustion reaction.

The aim of the present work was to determine the optimal conditions for synthesizing nanopowders of PSZD (3 mol.% Y_2O_3) by the glycine-nitrate method and regimes for obtaining ceramics with high mechanical strength from nanopowders by the SPS method.

The zirconium compound used was an oxynitrate $ZrO(NO_3)_2 \cdot 2H_2O$ (analytical grade, TU 6-09-1406–76); yttrium nitrate $Y(NO_3)_3 \cdot 6H_2O$ (chemical grade, TU 6-09-4676–83) was the compound of the stabilizing element (3 mol.% Y_2O_3). Glycine NH_2CH_2COOH (pure grade, GOST 5860–75) served as the organic precursor.

According to [6] the main synthesis parameters affecting the characteristics of c-ZrO_2 powders are the molar ratio of glycine to total NO_3^- (G/N) and the heat-treatment temperature of nanosize powders. The molar ratio G/N was calculated according to Eqs. (1) and (2).

Zirconium oxynitrate, yttrium nitrate and glycine were dissolved in distilled water. The solution of the water-organic precursor was evaporated at temperature 90 – 100°C in a vertical tubular furnace to the gel state, after which the temperature was raised to 250 – 300°C; in the process the gel burned, which was accompanied by rapid release of gaseous products of reaction, an increase in the volume of the system and the formation of 'ashes' (PSZD nanopowder). To elimi-

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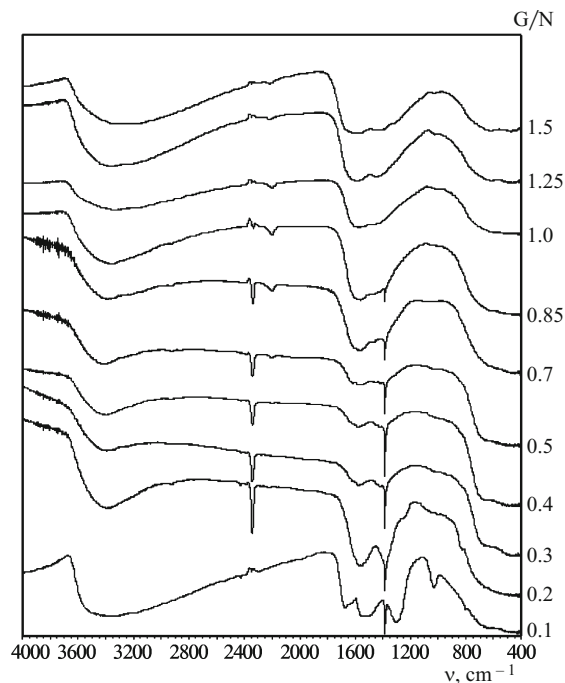[2] E-mail: chizh@rctu.ru.
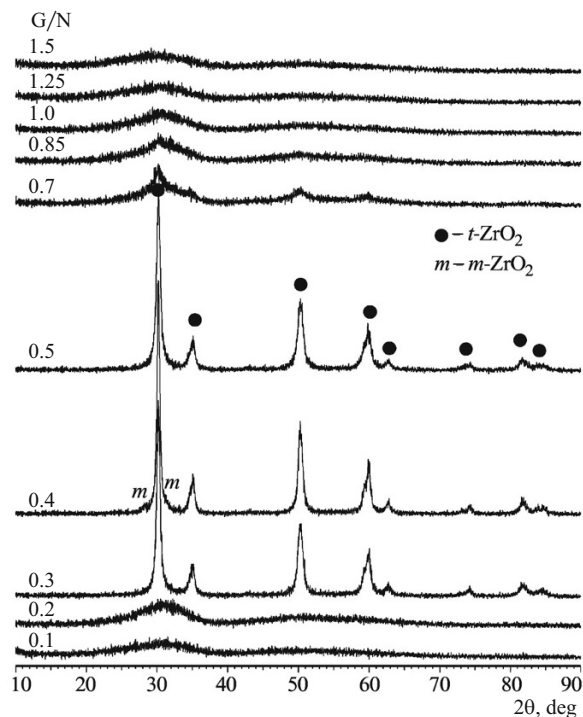
Fig. 1. Diffraction patterns of the initial synthesized powders before annealing. The numbers of the curves correspond to the glycine-to-nitrate molar ratio G/N.

Fig. 2. IR spectra of powders before annealing.

nate the nitrogen and carbon compounds and form the PSZD microstructure the 'ashes' were heat-treated in the temperature interval $400 - 850°C$. The powders obtained were disaggregated under soft conditions in a water medium in a Puverisette-5 (Fritsch) centrifugal planetary mill (rotation speed 150 min^{-1}, the drums and balls were made of PSZD) and dried at 70°C. After machining blanks ($40 \times 6 \times 4$ mm bars) were formed from the powder ($p_{sp} = 100 - 200$ MPa, temporary process binder — PVC) and annealed. The losses during heating of the initial zirconium and yttrium nitrates and the characteristics of the ceramic (apparent density, strength in bending and others) were determined by standard methods [7].

The initial compounds, powders and ceramic were studied by laser granulometry (Analysette-22 Economy, Fritsch), x-ray phase analysis (D2 PHASER diffractometer, Bruker) and differential-thermal analysis (EXSTAR TG/DTA 7300, SII), combined with mass-spectrometry (THERMOSTAR, Pfeiffer Vacuum) — DTA-TG/MS, IR spectroscopy (FSM 1201, Infraspek IR-FT Spectrometer), optical microscopy (POLAR-3, Mikromed) and electronic microscopy (VEGA III, Tescan). The specific surface of the powders was determined by low-temperature adsorption of nitrogen (Quadrasorb SI/Kr, Quantachrome). The annealing regime for blanks was determined by dilatometry (DIL 402 PC, NETZSCH).

The phases were identified by means of the JCPDS-PDF2 database. The average size of the crystallites

of the tetragonal phase of ZrO_2 powders was determined by means of the TOPAS 4.2 software.

DISCUSSION

The diffraction patterns of the initial powders, synthesized with different values of G/N before annealing, are presented in Fig. 1.

X-ray phase analysis shows that the glycine/nitrate molar ratio has a large effect on the degree of crystallinity of the structure of PSZD. For example, for low G/N ($0.1 - 0.2$) and high G/N (≥ 0.85) the synthesized powders are x-ray amorphous prior to annealing. For the average values of G/N (0.3 and 0.5) the powders are represented by crystalline tetragonal ZrO_2 (JCPDS No.79-1770), while about 8 wt.% m-ZrO_2 (JCPDS No. 13-0307) was found together with t-ZrO_2 in powder synthesized at G/N = 0.4.

We determined that, just as in [6], the molar ratio G/N has a significant effect on the content of the residual products of combustion in powders: as the ratio G/N increases from 0.1 to 1.5 the color of the initial PSZD powders changes from white to black.

The IR spectra of the PSZD powders before heat-treatment are virtually identical to those of c-ZrO_2 [6]. According to IR spectroscopy (Fig. 2) the following are present in the powders before heat-treatment: physically adsorbed CO_2 ($\nu = 1384$ cm^{-1}) and CO ($\nu = 2200$ cm^{-1}), bidentate bonded carbonate groups ($\nu \sim 1330$ cm^{-1} and ~ 1620 cm^{-1}), linearly coordinated CO_2 ($\nu = 2340$ cm^{-1}), O–H-bonds ($\nu = 3000 - 3600$ cm^{-1}) and Zr(Y)–O-bonds. In addition, the CO_2 content decreases and CO increases with increasing G/N.
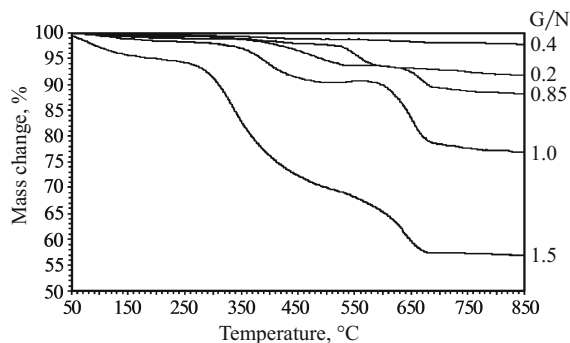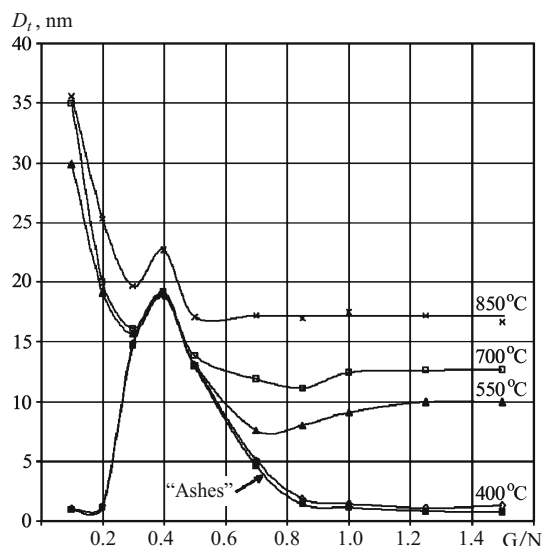
Fig. 3. TGA curves for powders before annealing.

Fig. 5. Photomicrograph of PSZD nanopowder after annealing.

Fig. 4. The effect of the synthesis regimes for powders on the size of t-ZrO_2 crystallites.

As expected, a temperature increase promotes carbon burn-out. According to the DTA/TG-MS data the complete removal of the products of combustion, just as in [6], occurs at about 700°C (Fig. 3).

Analysis of the effect of synthesis regimes (G/N, annealing temperature) on the sizes (D_t) of t-ZrO_2 crystallites in the powders makes it possible to judge the evolution of PSZD microstructure. In this connection and to eliminate residual carbon and nitrogen compounds the synthesized powders were heat-treated in the temperature interval 400 – 850°C. The isothermal soaking time $\tau_{i.s}$, unlike that in [6], was chosen to be 2 h rather than 24 h because with air being blown through the furnace this time is adequate for removing carbon and nitrogen compounds.

The results (Fig. 4) show that the annealing of PSZD powders at 400°C does not promote growth of crystallites: the dependence is identical to that for synthesized powder ('ashes'). The curves for G/N = 0.4 have an extremum corresponding to crystallite sizes about 19 nm. Such an extremum was also observed by the authors of [6] for 8YSZ powder, but the c-ZrO_2 crystallites were much smaller (≤ 8 nm).
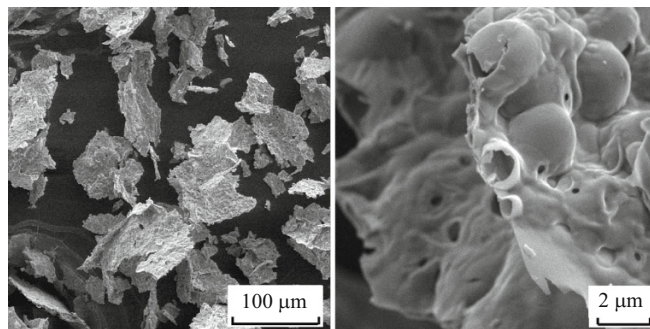
The results of annealing the powders show that the crystallization of the tetragonal phase of ZrO_2 is observed with temperature increasing to 550°C. It should be noted that the temperature dependences of the crystallite sizes versus G/N change practically symbatically.

The maximum crystallite sizes were obtained in PSZD powders synthesized at low values of G/N (0.1) after annealing at temperatures above 400°C: 30 nm (550°C) and about 35 nm (700, 850°C). As G/N increases to 1.0 with temperature also increasing the sizes of the crystallites in PSZD powders change in the following sequence: 10 nm (550°C), 13 nm (700°C) and 18 nm (850°C).

The PSZD powders annealed at temperature below 700°C (with the exception of the sample synthesized at G/N = 0.4) are single-phase: they are represented only by the tetragonal phase of ZrO_2. In powders synthesized at G/N = 0.4, after annealing about 8% m-ZrO_2 remains in the entire experimental temperature range. The monoclinic phase of ZrO_2 was also found in powders synthesized in the interval G/N = 0.2 – 0.5 and annealed at temperature 850°C.

The maximum size of crystallites at G/N = 0.4 in synthesized PSZD powders before and after annealing at 400°C is due to the highest burn temperature. In the opinion of the authors the decrease of the crystallite size for G/N > 0.4 is associated with a reduction of the burn temperature and (or) the presence of a significant quantity of carbon compounds in the products of synthesis.

Since the PSZD powders for mechanically strong ceramic ideally should be single-phase (t-ZrO_2), contain no carbon or nitrogen compounds and have crystallites with the minimum size, the ratio G/N = 0.85 and temperature 700°C were taken as the optimal conditions for synthesizing the powders.

The specific surface and bulk density of the PSZD powder synthesized under these conditions were 10.5 m^2/g and 0.035 g/cm^3. According to electron microscopy (Fig. 5) the PSZD powder is a nanocrystalline material: the porous agglomerates of floccular form, 50 – 100 µm long and 5 – 10 µm thick, consist of particles about 20 nm in size.

Optimization of the conditions for the disaggregation process made it possible to decrease the average size of the
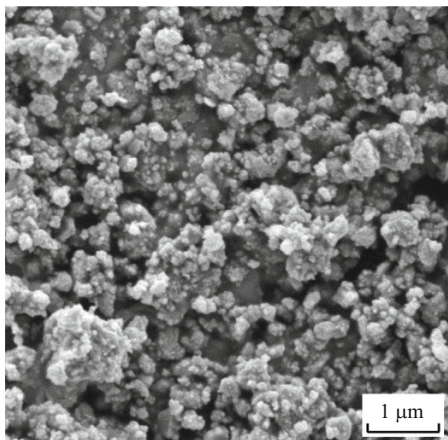
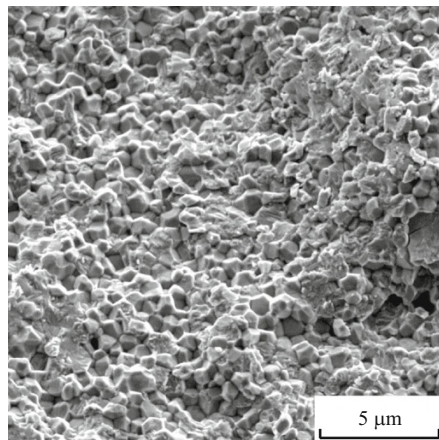**Fig. 6.** Photomicrograph of PSZD powder after disaggregation.

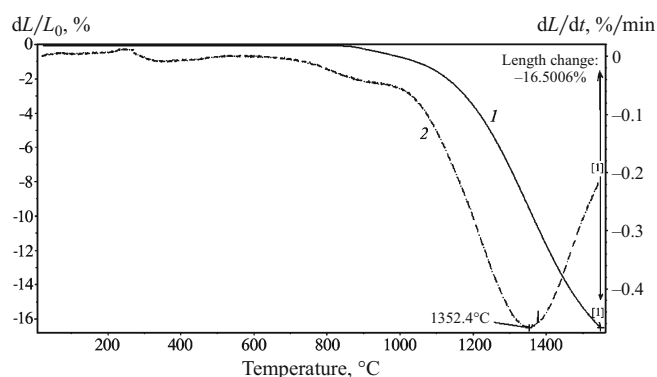**Fig. 8.** Photomicrograph of a cleavage surface of the ceramic.

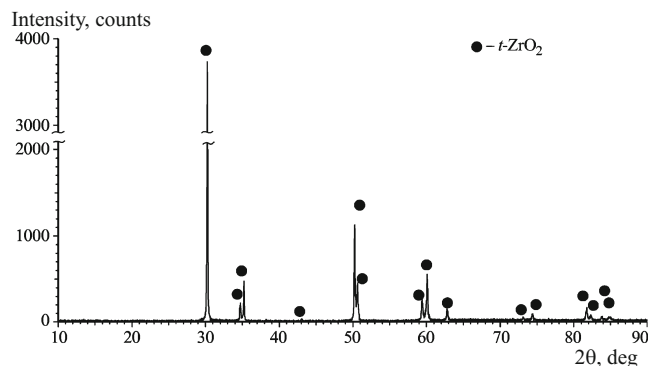**Fig. 7.** The shrinkage (*1*) and rate of shrinkage (*2*) versus temperature.

Fig. 9. Diffraction pattern of the ceramic.

aggregates in the PSZD powder from 26 to about 0.5 μm (Fig. 6).

Small bars were formed from the powders obtained under pressing pressure $100 - 200$ MPa by the SPS method. The annealing regime was determined on the basis of the results of dilatometric analysis (Fig. 7).

For heating rate 10 K/min the samples start to sinter at 900°C, the maximum rate of sintering is observed at 1350°C, and the process reaches completion at 1550°C.

The microstructure of the ceramic after annealing at 1550°C can be judged on the basis of a photomicrograph of a cleavage surface, shown in Fig. 8. The ceramic possesses equicrystallite microstructure: it consists of grains with average size $0.3 - 0.5$ μm. There is practically no closed porosity. XPA shows the ceramic to be single-phase; it is represented by the t-ZrO_2 phase only (Fig. 9).

The ceramic characteristics obtained — quite high apparent density $(5.90 - 5.95$ g/cm^3) and strength in bending $\sigma_b = 750 \pm 50$ MPa — attest to the fact that the glycine-nitrate method of synthesis yields PSZD powders from zirconium oxynitrate that are suitable (with optimization of the subsequent stages of the ceramic technology) for obtaining mechanically strong ceramic.

REFERENCES

1. E. S. Lukin, et al., "Modern oxide ceramic and applications," *Konstr. Kompozit. Mater.*, No. 1, 3 – 13 (2007).
2. E. V. Dudnik, Z. A. Zaitseva, A. V. Shevchenko, and L. M. Lopato, "Methods for obtaining disperse powders based on zirconium dioxide," *Poroshk. Metall.*, No. 7, 24 – 30 (1993).
3. E. S. Lukin, "Modern high-density oxide ceramic with regulatable microstructure," *Ogneup. Tekh. Keram.*, No. 9, 2 – 10 (1996).
4. S. V. Chizhevskaya, A. V. Zhukov, O. M. Klimenko, et al., "Obtaining nanostructured powders of partially stabilized zirconium dioxide for ceramic with high mechanical strength," *Steklo Keram*., No. 4, 18 – 21 (2010); S. V. Chizhevskaya, A. V. Zhukov, O. M. Klimenko, et al., "Obtaining nanostructured powders of partially stabilized zirconium dioxide for ceramic with high mechanical strength," *Glass Ceram.*, **67**(3 – 4), 114 – 117 (2010).
5. S. V. Chizhevskaya, A. M. Chekmarev, and O. M. Klimenko, "Obtaining mechanically strong construction ceramic based on partially yttrium-stabilized zirconium dioxide," in: *Proc. Sci. Tech. Conf. on Scientific Innovative Collaboration* [in Russian], Moscow (2002), Pt. 3, p. 48.
6. I. Kaus, P. I. Dahl, J. Mastin, et al., "Synthesis and characterization of nanocrystalline YSZ powder by smoldering combustion synthesis," *J. Nanomaterials*, Article ID 49283, pp. 1 – 7 (2006).
7. N. T. Andrianov, A. V. Belyakov, A. S. Vlasov, et al., *Practical Course in Technical Ceramics* [in Russian], Stroimaterialy, Moscow (2005).